Hydrogen in mechanically prepared nanostructured h-BN: a critical comparison with that in nanostructured graphite

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Hydrogen in mechanically prepared nanostructured h-BN: a critical comparison with that in nanostructured graphite

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Nanostructured h-BN was prepared by mechanical milling under hydrogen atmosphere. The hydrogen concentration reaches up to 2.6 mass% after milling for 80 h, and this value corresponds to ca. 35% of that of nanostructured graphite as was previously reported. In addition to the hydrogen desorption starting at about 570 K, nitrogen desorption was also detected at about 700 K. There was no recrystallization phenomenon at least below 1173 K. The dissimilarities on the (de-)hydriding properties between nanostructured h-BN and graphite might be due to the different local electronic structure near the specific defects. © *2002 American Institute of Physics.*
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The studies on carbon-hydrogen systems have been of great interest from the viewpoint of hydrogen storage[1,2] and gained recently further attention due to the discovery of new carbon-related nanostructures, such as nanotubes, nanofibers, etc.[3–11]

So far, we have studied the (de-)hydriding properties of nanostructured graphite prepared by mechanical milling under hydrogen atmosphere.[12–14] The hydrogen concentration reaches up to 7.4 mass% ($CH_{0.95}$) after milling for 80 h, and two desorption peaks of hydrogen molecule (mass number $=2$), starting at about 600 K and 950 K, respectively, are observed in thermal desorption mass spectroscopy. The first desorption peak has, in our opinion, a similar origin to the main peak of hydrogen desorption from the pre-treated single-walled carbon nanotubes,[15,16] in which defects for trapping hydrogen seem also to be formed.[17] Below the temperature of the second desorption peak, at which recrystallization related desorption occurs, the nanostructured graphite is expected to retain its specific defects and defective structures.

The experimental results mentioned above indicate that the specific defects and defective structures might provide the suitable trapping sites for hydrogen storage, and consequently affect the (de-)hydriding properties of nanostructured graphite.

Just recently we focus on the (de-)hydriding properties of mechanically prepared nanostructured hexagonal-(h-)BN, in order to obtain further insight into the relationship between the defective structures and (de-)hydriding properties of carbon-related materials. The h-BN compounds are known to possess a similar layer-structure and almost identical cell dimensions to that of graphite.[18] Based on such similarities, many research efforts have been theoretically and experimentally directed to various counterparts of carbon-related materials, such as B–N and B–C–N nanotubes.[19–26] It should be, however, emphasized that the Pauling's electronegativities (EN_{Pauling}) of the component elements are rather different; a higher $EN_{\text{Pauling}}=3.0$ for nitrogen compared with $EN_{\text{Pauling}}=2.0$ for boron in h-BN, instead of $EN_{\text{Pauling}}=2.5$ for carbon homogeneously in graphite. Therefore we expect that, due to the dissimilar local electronic structure, the (de-)hydriding properties of nanostructured h-BN would also be different than that of nanostructured graphite.

In this report, we present some preliminary experimental results on the nanostructure and (de-)hydriding properties of the mechanically prepared nanostructured h-BN. The (de-)hydriding properties of BN-based materials have not been studied so far, neither experimentally nor theoretically.

First, h-BN powder (purity$>$99%, $\sim$10 μm) was heated and evacuated for 10 h below 1×10^{-4} Pa by using a turbo molecular pump. Then the pre-treated powder was used for the sample preparation procedure, as described in Ref. 12, in which special caution had been taken to minimize the oxygen and water-adsorption.

The as-prepared samples were characterized by x-ray diffraction measurement (XRD, Mac Science MXP3, Cu$K\alpha$ radiation), Raman spectroscopy (Nicolet, Almega -HD, 532 nm laser with backscattering geometry), oxygen-combustion hydrogen analysis (OCHA, Perkin Elmer 2400 II), thermogravimetry and differential thermal analysis (TG and DTA, Seiko TG8120), and thermal desorption mass-spectroscopy (TDS, ANELVA M-QA200TS). Here, the thermal analysis apparatus were specially designed and installed, so that the measurements of TG, DTA, and TDS could be achieved simultaneously without exposing the samples to air. In the thermal analyses measurement, high-purity helium (purity $>$99.9999%) was adopted as a carrier gas, and the heating rate was 10 K/min.

Figure 1 presents the XRD profiles of h-BN mechanically milled for different times. The long-range ordering of h-BN gradually disappears with increasing milling time, and no diffraction peak could be observed after milling longer than 15 min. A similar behavior was also detected when graphite was subjected to the identical milling process, ex-

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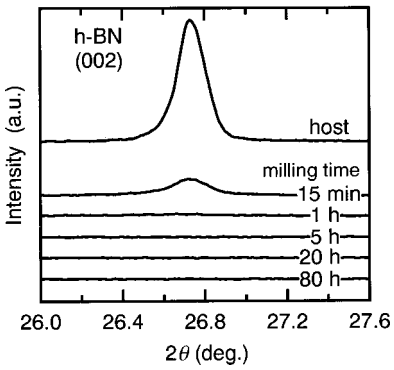

FIG. 1. X-ray (002) diffractions of the host and nanostructured h-BN mechanically milled under initial hydrogen pressure of 1.0 MPa at room temperature.

cept that a longer milling time was needed before the diffraction peak disappeared, which is probably due to the stronger inter-layer interaction in graphite.[27]

The in-layer nanostructure was studied by Raman spectroscopy, and the result of which is shown in Fig. 2. Similar to nanostructured graphite, the high-frequency in-layer E_{2g} mode for nanostructured h-BN broadens and shifts to higher frequencies. Estimated from the full width at half maximum (FWHM) of the E_{2g} modes,[28] the in-layer crystallite size decreases from >30 nm for the host sample to less than 10 nm after milling for 5 h, and finally reached down to ~ 3 nm after 80 h. The crystallite size after 80 h is quite comparable to that of the nanostructured graphite.[13,14]

As shown in Fig. 3, the total hydrogen concentration in h-BN determined by OCHA reaches up to 2.6 mass% after

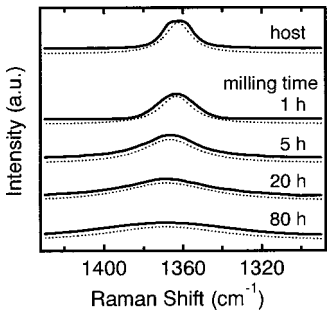

FIG. 2. Raman spectra of the host and nanostructured h-BN mechanically milled under hydrogen atmosphere. The dotted lines indicate the Lorenzian approximations.

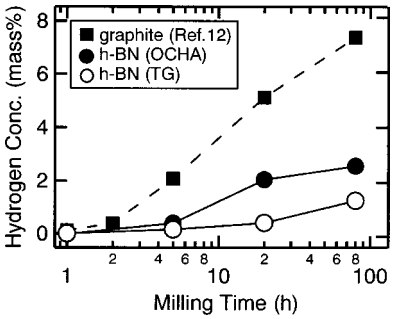

FIG. 3. Hydrogen concentrations in nanostructured h-BN and graphite mechanically milled for different times. Closed marks indicate the total hydrogen concentrations determined by OCHA, and open marks the partial hydrogen concentrations desorbed below 1173 K determined by TG.

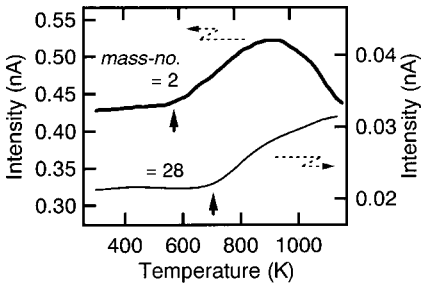

FIG. 4. TDS spectra of nanostructured h-BN mechanically milled under hydrogen atmosphere for 80 h. The solid arrows indicate the temperature from which the hydrogen and nitrogen desorptions start. The heating rate is 10 K/min.

milling for 80 h, which is only ca. 35% of the corresponding value of the nanostructured graphite.[12,14] The significant difference in the hydrogen concentration is most likely due to the different local electronic structure near the specific defects. In contrast to the pure covalent C–C bond, B–N bond is *polar* covalent originated from the different EN_{Pauling} as mentioned above.[27] This partial ionic character determines the low density of unpaired electron near the specific defects, and therefore, the concentration of hydrogen that is dominantly trapped near the specific defects is expected to be lower than that in the nanostructured graphite.

Two kinds of gas-phase product with mass numbers $=2$ and 28, starting to desorb at about 570 K and 700 K, respectively, were detected by TDS measurements, as was shown in Fig. 4. The former surely corresponds to hydrogen molecule, and the starting temperature for desorption is quite close to that of the nanostructured graphite, ca. 600 K.[14] The latter is nitrogen molecule formed by decomposition of the nanostructured h-BN.

A weight-loss corresponding to the hydrogen and nitrogen desorptions was synchronously detected by TG measurements. As shown in Fig. 5, the hydrogen concentrations estimated from the weight-losses in TG measurements were much less than the corresponding values determined by OCHA shown in Fig. 3. This difference revealed that a part of hydrogen was still strongly trapped in the nanostructured h-BN even after being heated up to 1173 K, in contrast to the case of the nanostructured graphite.[14] Correspondingly, no recrystallization of nanostructure h-BN was detected by DTA (shown in Fig. 5) and XRD (not shown here) measurements, i.e., h-BN retained its defective nanostructure at least below 1173 K, while hydrogen desorption related recrystallization

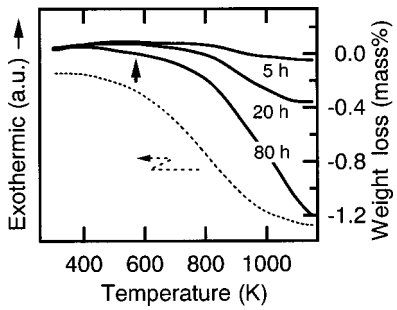

FIG. 5. TG profiles of nanostructured h-BN mechanically milled under hydrogen atmosphere for different times, and DTA profile of the 80 h sample (in dashed line). The solid arrow corresponds to the hydrogen desorption temperature shown in Fig. 4. The heating rate is 10 K/min.

started at about 950 K for nanostructured graphite.[14]

Nanostructured h-BN, similar to nanostructured graphite, possesses the ability to trap(absorb) hydrogen during the milling process and to desorb hydrogen at elevated temperatures. More importantly, it could be shown in the present work that the (de-)hydriding properties depend not only on the defective nanostructure itself, but also on the local electronic structure near the specific defects. This information provides a constructive perspective for the design of new carbon-related materials for hydrogen storage.

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[1] C. Carpetis and W. Peschka, Int. J. Hydrogen Energy **5**, 539 (1980).
[2] K. A. G. Amankwah, J. S. Noh, and J. A. Schwarz, Int. J. Hydrogen Energy **14**, 437 (1989).
[3] A. C. Dillon, K. M. Jones, T. A. Bekkedahl, C. H. Kiang, D. S. Bethune, and M. J. Heben, Nature (London) **386**, 377 (1997).
[4] A. C. Dillon and M. J. Heben, Appl. Phys. A: Mater. Sci. Process. **72**, 133 (2001).
[5] Y. Ye, C. C. Ahn, C. Witham, B. Fultz, J. Liu, A. G. Rinzler, D. Colbert, K. A. Smith, and R. E. Smalley, Appl. Phys. Lett. **74**, 2307 (1999).
[6] A. Chambers, C. Park, P. T. K. Baker, and N. M. Rodriguez, J. Phys. Chem. B **102**, 4253 (1998).
[7] C. Park, P. E. Anderson, A. Chambers, C. D. Tan, R. Hidalgo, and N. M. Rodriguez, J. Phys. Chem. B **103**, 10572 (1999).
[8] C. C. Ahn, Y. Ye, B. V. Ratnakumar, C. Witham, R. C. Bowman, Jr., and B. Fultz, Appl. Phys. Lett. **73**, 3378 (1998).
[9] L. Schlapbach, A. Züttel, P. Gröning, O. Gröning, and P. Aebi, Appl. Phys. A: Mater. Sci. Process. **72**, 245 (2001).
[10] V. Meregalli, M. Parrinello, Appl. Phys. A: Mater. Sci. Process. **72**, 143 (2001).
[11] A. Züttel, Ch. Nützenadel, P. Sudan, Ph. Mauron, Ch. Emmenegger, S. Rentsch, L. Schlapbach, A. Weidenkaff, and T. Kiyobayashi, J. Alloys Compd. (in press).
[12] S. Orimo, G. Majer, T. Fukunaga, A. Züttel, L. Schlapbach, and H. Fujii, Appl. Phys. Lett. **75**, 3093 (1999).
[13] T. Fukunaga, K. Itoh, S. Orimo, M. Aoki, and H. Fujii, J. Alloys Compd. **327**, 224 (2001).
[14] S. Orimo, T. Matsushima, H. Fujii, T. Fukunaga, and G. Majer, J. Appl. Phys. **90**, 1545 (2001).
[15] A. C. Dillon, T. Gennett, J. L. Alleman, K. M. Jones, P. A. Parilla, and M. J. Heben, Proceedings of the 2000 DOE/NREL Hydrogen Program Review, 8–10 May 2000.
[16] M. Hirscher, M. Becher, M. Haluska, U. Dettlaff-Weglikowska, A. Quintel, G. S. Duesberg, Y.-M. Choi, P. Downes, M. Hulman, S. Roth, I. Stepanek, and P. Bernier, Appl. Phys. A: Mater. Sci. Process. **72**, 129 (2001).
[17] M. Monthioux, B. W. Smith, B. Burteaux, A. Claye, J. E. Fischer, and D. E. Luzzi, Carbon **39**, 1251 (2001).
[18] N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements* (Pergamon, Hong Kong, 1984).
[19] A. Rubio, J. L. Corkill, and M. L. Cohen, Phys. Rev. B **49**, 5081 (1994).
[20] N. G. Chopra, R. J. Luyken, K. Cherrey, V. H. Crespi, M. L. Cohen, S. G. Louie, and A. Zettl, Science **269**, 966 (1995).
[21] A. Loiseau, F. Willaime, N. Demoncy, G. Hug, and H. Pascard, Phys. Rev. Lett. **76**, 4737 (1996).
[22] A. Y. Liu, R. M. Wentzcovitch, and M. L. Cohen, Phys. Rev. B **39**, 1760 (1989).
[23] K. Esfarjani, K. Ohno, and Y. Kawazoe, Phys. Rev. B **50**, 17830 (1994).
[24] X. Blase, J.-C. Charlier, A. De Vita, and R. Car, Appl. Phys. Lett. **70**, 197 (1997).
[25] O. Stephan, Y. Bando, C. Dussarrat, K. Kurashima, T. Sasaki, T. Tamiya, and M. Akaishi, Appl. Phys. Lett. **70**, 2383 (1997).
[26] Ph. Kohler-Redlich, M. Terrones, C. Manteca-Diego, W. K. Hsu, H. Terrones, M. Rühle, H. W. Kroto, and D. R. M. Walton, Chem. Phys. Lett. **310**, 459 (1999).
[27] A. Catellani, M. Posternak, A. Baldereschi, and A. J. Freeman, Phys. Rev. B **36**, 6105 (1987).
[28] R. J. Nemanich, S. A. Solin, and R. M. Martin, Phys. Rev. B **23**, 6348 (1981).